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(54)【発明の名称】　リチウム二次電池

(57)【要約】
【課題】　特に高い充放電電流で充放電を行った場合のリチウムの吸蔵・放出量が多くて充放電容量が大きく、かつ充放電サイクルによる充放電容量の低下が少ないリチウム二次電池を低コストで得る。
【解決手段】　リチウムイオンを吸蔵・放出する炭素質物からなる負極と正極と非水電解液を有するリチウム二次電池において、炭素質物としてカサ比重が異なる２種以上の黒鉛質粒子を含むものを用いる。

【特許請求の範囲】

【請求項１】　リチウムイオンを吸蔵・放出する炭素質物からなる負極と正極と非水電解液を有するリチウム二次電池において、前記炭素質物が、カサ比重が異なる２種以上の黒鉛質粒子を含むことを特徴とするリチウム二次電池。

【請求項２】　炭素質物が、カサ比重が０．４～０．６５の範囲にある黒鉛質粒子とカサ比重が０．８５～１．３０の範囲にある黒鉛質粒子とからなる請求項１記載のリチウム二次電池。

【請求項３】　カサ比重が０．８５～１．３０の範囲の黒鉛質粒子の結晶の層間距離ｄ（００２）が０．３３８ｎｍ以下、Ｃ軸方向の結晶子サイズＬｃ（００２）が５０ｎｍ以上、平均粒径が１０～１００μｍ、比表面積が０．３～２．０m^2／ｇ、アスペクト比が１．１～５であり、且つ該黒鉛質粒子の構造が、偏平状の粒子を複数集合又は結合してなる黒鉛質粒子である請求項２記載のリチウム二次電池。

【請求項４】　カサ比重が０．８５～１．３０の範囲の黒鉛質粒子が、少なくとも黒鉛化可能な骨材と黒鉛化可能なバインダを混合する工程、該混合物を５００～２０００℃で焼成する工程、該焼成物を平均粒径１０～１００μｍに粉砕する工程及び該粉砕物を２５００℃以上で黒鉛化する工程を有する製造法で製造された黒鉛質粒子である請求項２記載のリチウム二次電池。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、リチウム二次電池に関し、特に充放電容量、急速充放電特性、サイクル特性に優れたリチウム二次電池に関する。

【０００２】

【従来の技術】近年、ポータブル機器、電気自動車、電力貯蔵用として小型、軽量で高エネルギー密度を有する二次電池に対する要望が高まっている。このような要望に対し、非水系電解液二次電池、特にリチウム二次電池はとりわけ高電圧、高エネルギー密度を有する電池として注目を集めている。

【０００３】リチウム二次電池の負極材料としては、金属リチウム、低黒鉛化炭素粒子、高黒鉛化炭素粒子が使用されている。金属リチウムは高い充放電容量を実現可能であるが、その高い反応性のため充放電サイクルの経過と共に電解液中の溶媒と反応し容量が低下する。また、樹枝状の金属リチウムが生成しやすく、正・負極間に設けられるセパレータを貫通し短絡を引き起こしやすいという問題点を有している。低黒鉛化炭素質材料は、電解液との反応性が低い、樹枝状金属リチウムが生成しずらいという特徴を有するが、充放電容量が一般に低く、また真密度が低いため体積当たりの充放電容量が低いという難点を有し、高エネルギー密度の二次電池を実現することは達成されていない。一方、高黒鉛化炭素粒子は、低黒鉛化炭素粒子と比較して高い充放電容量を有し、金属リチウムと比較して電解液との反応性、樹枝状金属リチウムが生成しずらいという特徴を有することから、近年、負極用材料として盛んに検討がなされるようになってきている。

【０００４】高黒鉛化炭素粒子としては、高純度化された天然黒鉛質粒子、コークスやピッチあるいは合成有機高分子材料を炭化・黒鉛化して製造される人造黒鉛質粒子が使用されている。これらの高黒鉛化炭素質粒子では、黒鉛結晶が高度に発達しているため、形状はアスペクト比の大きな鱗片状をしている。このため、バインダと混練して集電体に塗布して電極を作製した場合、鱗片状の黒鉛質粒子が集電体の面方向に高密度に配向し、その結果、負極層内への電解液の浸透性が悪化し充放電容量が低下、高速充放電特性が低下する、黒鉛質粒子へのリチウムの吸蔵・放出の繰り返しによって発生する厚さ方向の歪みにより粒子が剥離しやすいためサイクル特性が悪いなどの問題が発生する。一方、上記のような問題を回避するため、電極中の黒鉛質粒子の密度を低下させると体積当たりの充放電容量が低下するという問題が発生する。

【０００５】このような問題を解決する手法として、高黒鉛化粒子の特性の改善が試みられている。特許２６３７３０５号明細書では、メソフェーズピッチから抽出されたメソフェーズ小球体を黒鉛化して得られた球状で微細組織の配向が放射状あるいはブルックスーテーラー型の黒鉛化粒子、及び微細組織の配向がラメラ型又はブルックスーテーラー型の炭素繊維を用いることを提案しているが、前者は充放電容量が２８０～３００ｍＡｈ／ｇと比較的低く、またメソフェーズピッチからの抽出、分離という工程が必要なため高コストであり、後者は電極の高密度化が困難、また長繊維が混在するとセパレータを貫通し短絡が起こりやすいという問題がある。特開平７－３３５２１６号公報には、骨材及び結合材を出発原料として作製された高密度黒鉛成形体を粉砕して製造される黒鉛結晶子がランダムに配向した粒子が提案されているが、冷間静水圧成形法を用いる成形体の製造方法は生産性に乏しい。黒鉛化された成形体を粉砕して黒鉛質粒子を得る方法としては、この他に再公表特許ＷＯ９５／２８０１１号公報及び特開平９－２３１９７４号公報に記載された方法が挙げられる。これらの黒鉛化成形体を粉砕して得られる黒鉛粉末はいずれも高密度が高く高強度であり、黒鉛結晶が粒子内でランダムに配向しているため、集電体上での黒鉛結晶の配向が抑制され、また電解液が浸透できる粒子間の空隙が確保されるという点で有効な手段である。しかしながら、粒子が高カサ比重、すなわち緻密質であるということが、今度は粒子内への電解液の浸透を抑制し、急速充放電特性の向上に限界を生じさせる原因となっている。この問題を解決する方法として、発明者らは特開平１０－１５８００５号公

報等において、偏平状の黒鉛質粒子が複数互いに非平行に集合あるいは結合した黒鉛質粒子であり、０．１～１００μmの範囲に０．４～２．０cc／gの細孔を有する黒鉛質粒子を提案した。このような黒鉛質粒子は上の高嵩密度黒鉛質粒子の課題であった粒子内部への電解液の浸透が実現されるため、極めて優れた急速充放電特性を示すものであるが、低嵩密度粒子であることが今度は電極成形条件によっては黒鉛質粒子の変形、その結果としての配向が発生しやすく充放電サイクル特性が劣化する問題があり、負極作製の作業条件が限定されていた。

【０００６】高黒鉛化炭素粒子と他の材料を混合して使用する技術が提案されている。特開平４－２３７９７１号公報では、球状の黒鉛質炭素粒子と炭素繊維とを組み合わせることによって、充放電の繰り返しによる粒子の剥離を防止することが提案されているが、球状以外の高黒鉛化炭素粒子については言及されていない。特開平６－３６７６０号公報では、高黒鉛化炭素粒子と低黒鉛化炭素粒子の混合物を用いることによって放電末期の急速な電圧降下を防止し電池容量の終点判定を容易とすることが提案されているが、高黒鉛化粒子の集電体面方面への配向については言及されておらず、また低黒鉛化炭素粒子の添加量が多い場合は放電電圧が低下するため添加量には３０容量%という上限が設けられている。特開平６－１１１８１８号公報では球状黒鉛化炭素粒子と黒鉛化炭素短繊維を組み合わせることを提案しており、電極強度を増加させ充放電サイクルに伴う電極層の破壊の抑制、短繊維による電極層内の導電性向上による急速充放電特性の改善が図れるとしているが、球状黒鉛化炭素粒子以外の高黒鉛化炭素粒子についての言及はなされておらず、また黒鉛化炭素短繊維の添加量が多い場合には電極密度が低下し、体積当たりの充放電容量が低下するため黒鉛化炭素短繊維の添加量には３０容量%という上限が設けられている。特開平６－３０２３１５号公報では球状黒鉛質粒子と化学的、電気化学的に不活性な金属被覆ウィスカーを組み合わせることにより電極を高強度化し粒子の剥離を防止することが提案されているが、球状以外の黒鉛質粒子についての言及はなく、また添加するウィスカーには充放電には寄与しないため添加量が多い場合には充放電容量の低下が発生することは明かである。特開平８－１８０８６４号公報には球状黒鉛質粒子とこの球状粒子の平均粒径に対して１．３～４．０の比の平均粒径を有する非球状黒鉛質粒子及び炭素繊維粉砕物を添加することにより、電極内の電子伝導性が向上し充放電サイクル特性が改善される旨の記載がある。この中で、非球状粒子（人造黒鉛、天然黒鉛）が球状黒鉛質粒子の間に様々な方向を向いて存在するということが言及されており、上記の鱗片状黒鉛質粒子の集電体面方向への配向を抑制するということに対して球状黒鉛質粒子の存在が効果を有することが示されているが、球状粒子と非球状粒子の粒子径を精密に制御する必要があり、生産性という点で問題がある。特開平８－８３６０８号公報、特開平８－８３６０９号公報にはブロック状、フレーク状及び粒状の人造黒鉛又は天然黒鉛質粒子に黒鉛化した炭素繊維粉末を添加することにより、高密度で黒鉛結晶が集電体面方向に配向しずらく、充放電サイクル経過に伴う集電体からの粒子の剥離が抑制される旨の記載がある。しかし、この効果が得られるのは黒鉛化炭素繊維粉末添加量が２０重量%までであり、これ以上では電極性能が低下することが言及されている。

【０００７】以上に示した高黒鉛化炭素質粒子と他の材料の混合系では、それぞれ問題を有しており、また特に黒鉛化炭素繊維と組み合わせる場合、粒子形状が大きく異なるため均一に混合することが困難であり、このためそれぞれの特許公開公報で示されている添加量の上限を超えた部分が発生する可能性があり、安定化したリチウム二次電池の製造が困難であるという共通の問題がある。また、メソフェーズ小球体を黒鉛化して得られた球状黒鉛質粒子を含む系については上で述べたようにこの球状黒鉛質粒子の充放電容量が比較的低い、かつ高コストであるという問題点を有している。

【０００８】

【発明が解決しようとする課題】本発明の目的は、特に高い充放電電流で充放電を行った場合のリチウムの吸蔵・放出量が多くて充放電容量が大きく、かつ充放電サイクルによる充放電容量の低下が少ないリチウム二次電池を低コストで得ることにある。

【０００９】

【課題を解決するための手段】本発明は、リチウムイオンを吸蔵・放出する炭素質物からなる負極と正極と非水電解液を有するリチウム二次電池において、前記炭素質物が、カサ比重が異なる２以上の黒鉛質粒子を含むことを特徴とするリチウム二次電池に関する。

【００１０】本発明は、また、前記炭素質物が、カサ比重が０．４～０．６５の範囲にある黒鉛質粒子とカサ比重が０．８５～１．３０の範囲にある黒鉛質粒子とからなる前記リチウム二次電池に関する。

【００１１】本発明は、また、前記カサ比重が０．８５～１．３０の範囲の黒鉛質粒子の結晶の層間距離d（００２）が０．３３８nm以下、C軸方向の結晶子サイズLc（００２）が５０nm以上、平均粒径が１０～１００μm、比表面積が０．３～２．０m²／g、アスペクト比が１．１～５であり、且つ該黒鉛質粒子の構造が、偏平状の粒子を複数集合又は結合してなる黒鉛質粒子である前記リチウム二次電池に関する。

【００１２】本発明は、また、前記カサ比重が０．８５～１．３０の範囲の黒鉛質粒子が、少なくとも黒鉛化可能な骨材と黒鉛化可能なバインダを混合する工程、該混合物を５００～２０００℃で焼成する工程、該焼成物を平均粒径１０～１００μmに粉砕する工程及び該粉砕物を２５００℃以上で黒鉛化する工程を有する製造法で製

造された黒鉛質粒子である前記リチウム二次電池に関する。

【００１３】

【発明の実施の形態】以下に本発明について詳述する。

【００１４】本発明で用いられる負極用炭素質物は、カサ比重が異なる２以上の黒鉛質粒子からなっている。ここで述べるカサ比重とは、ＪＩＳ　Ｋ－１４６９に記載される方法で測定される値である。１種類のカサ比重の小さな黒鉛質粒子を用いた場合、電極の作製条件によっては粒子が過剰に変形し黒鉛結晶が集電体の面方向に配向しやすく、サイクル特性、急速充放電特性が劣化し、充放電容量が低下し易い。一方１種類のカサ比重が大きい黒鉛質粒子を用いた場合、粒子内への電解液の浸透が不十分であり、急速充放電特性が低下する。負極用炭素質材料を構成する黒鉛質粒子としては、少なくとも一つはカサ比重が０．４～０．６５の範囲にある黒鉛質粒子を含むことが好ましく、０．４～０．６５の範囲にある黒鉛質粒子とカサ比重が０．８５～１．３０の範囲にある黒鉛粒子を併用することが好ましい。前者の黒鉛質粒子のカサ比重がその下限を下回った場合、電極作製に用いるスラリーの粘度が高くなる傾向があり、バインダ添加量を多くする必要がある等の理由から好ましくない。一方、前者の黒鉛質粒子のカサ比重がその上限を超えた場合、急速充放電特性が低下する傾向がある。後者の黒鉛質粒子のカサ比重がその下限を下回った場合、電極作製条件による黒鉛質粒子の過剰な変形が起こり易く、サイクル特性及び急速充放電特性が低下する傾向がある。後者のカサ比重がその上限を超えた場合、急速充放電特性が低下する傾向がある。カサ比重の異なる２以上の黒鉛質粒子の配合比については本発明では特に制限せず、目的とするリチウム二次電池の設計に合わせて選択されるが、好ましくは、前者を４０～９５重量%、後者を５～６０重量%使用する。

【００１５】負極を構成するカサ比重の異なる２以上の黒鉛質粒子のいずれの（００２）面の格子面間隔ｄ（００２）、Ｃ軸方向の結晶子サイズＬｃ（００２）、真密度はそれぞれ０．３３８ｎｍ以下、５０ｎｍ以上、２．２１ｇ／ｃm^3以上とすることが好ましい。それぞれより好ましくは０．３３５～０．３３８ｎｍ、６０ｎｍ以上とする。それぞれの充放電容量はほぼ等しいことが適当であり、好ましくは３００ｍＡｈ／ｇ以上、より好ましくは３３０ｍＡｈ／ｇ以上とし、更に黒鉛質粒子間のその差は１０%以下、より好ましくは５%以下とする。これにより充放電容量の変化（低下）を伴わずにカサ比重の異なる２種以上の黒鉛質粒子を組み合わせた効果を得ることができる。また、カサ比重が０．４～０．６５の範囲の黒鉛質粒子は、水銀圧入法で測定される０．０１～１００μｍの範囲に細孔を有していることが好ましく、その値は０．４ｃｃ／ｇ～２．０ｃｃ／ｇの範囲が好ましい。また、負極を構成するカサ比重の異なる２以上の黒鉛質粒子の形状はほぼ等しいことが適当であり、好ましくはアスペクト比は１．１～５である。これにより、カサ比重の異なる２種以上の黒鉛質粒子を組み合わせて負極を構成した場合、これらの黒鉛質粒子の均一な分布が容易に実現され、ばらつきの少ない良好なリチウム二次電池を得ることができる。更に負極を構成するカサ比重の異なる２以上の黒鉛質粒子の比表面積に関し、カサ比重が、０．４～０．６５の範囲の黒鉛質粒子では２．０～５．０m^2／ｇであり、一方カサ比重が０．８５～１．３０の範囲の黒鉛質粒子では０．３～２．０m^2／ｇの範囲とすることが好ましく、これによってカサ比重の異なる２種以上の黒鉛質粒子を組み合わせて負極を作製しても不可逆容量の増加を伴わず、また負極を作製する際に使用する黒鉛質粒子とバインダと溶媒の混合物の粘度の変化を最小限とすることができる。更に負極を構成するカサ比重の異なる２種以上の黒鉛質粒子の粒子構造に関し、偏平状の粒子を複数集合又は結合してなる黒鉛質粒子であることが好ましい。本発明において、偏平状の粒子とは、長軸と短軸を有する形状の粒子のことであり、完全な球状でないものをいう。例えば鱗状、鱗片状、一部の塊状等の形状のものがこれに含まれる。この黒鉛質粒子において偏平状の粒子は集合又は結合しているが、結合とは互いの粒子が、タール、ピッチ等のバインダを炭素化した炭素を介して、化学的に結合している状態をいい、集合とは互いの粒子が化学的に結合していないが、その形状に起因して、その集合体としての形状を保っている状態をいう。機械的な強度の面から、結合しているものが好ましい。また黒鉛質粒子の偏平状の粒子の集合又は結合の状態としては、偏平状の粒子の配向面が非平行となるように集合又は結合している黒鉛質粒子を含むことが好ましい。ここで、偏平状の粒子の配向面が非平行とは、それぞれの粒子の形状において有する偏平した面、換言すれば最も平らに近い面を配向面として、複数の偏平状の粒子がそれぞれの配向面を一定の方向にそろうことなく集合している状態をいう。

【００１６】黒鉛質粒子の構造を上記にようにすることで、作製するリチウム二次電池の急速充放電特性及びサイクル特性をより向上させることが可能となる。

【００１７】本発明のカサ比重が異なる２種以上の黒鉛質粒子を含むことを特徴とするリチウム二次電池の負極に用いられる黒鉛質粒子の内、カサ比重が０．４～０．６５の範囲の黒鉛質粒子は、黒鉛化可能な骨材又は黒鉛と黒鉛化可能なバインダに黒鉛化触媒を１～５０重量%添加して混合し、焼成・黒鉛化した後、粉砕して製造される。黒鉛化可能な骨材としては、フルードコークス、ニードルコークス等の各種コークス類が使用可能である。また、天然黒鉛や人造黒鉛などの既に黒鉛化されている骨材を使用しても良い。黒鉛化可能なバインダとしては、石炭系、石油系、人造等の各種ピッチ、タールが使用可能である。黒鉛化触媒としては、鉄、ニッケル、

チタン、ホウ素、珪素等、これらの酸化物、炭化物、窒化物等が使用可能である。黒鉛化可能な骨材又は黒鉛と黒鉛化可能なバインダに黒鉛化触媒を１～５０重量％添加する。黒鉛化可能な骨材又は黒鉛、黒鉛化可能なバインダ及び黒鉛化触媒の配合比は、目的とする黒鉛質粒子の特に細孔容積に合わせて選択される。更に黒鉛化触媒については、その添加量が１重量％未満であると黒鉛質粒子の結晶の発達が悪くなり、充放電容量が低下する。一方、５０重量％を超えると、均一に混合することが困難となり、作業性の悪化及び得られる黒鉛質粒子の特性のばらつきが大きくなるため好ましくない。

【００１８】黒鉛化可能な骨材又は黒鉛化可能なバインダに黒鉛化触媒を１～５０重量％添加して混合し、焼成し、黒鉛化を行う。焼成の前に、必要に応じて前記混合物を適当な形に成形しても良い。焼成は前記混合物が酸化しがたい雰囲気で行うことが好ましく、例えば窒素雰囲気中、アルゴンガス中、真空中で焼成する方法が挙げられる。黒鉛化の温度は２０００℃以上が好ましく、２５００℃以上であることがより好ましく、２８００℃以上であることが更に好ましい。黒鉛化温度が低いと、黒鉛の結晶の発達が悪くなると共に、黒鉛化触媒が作製した黒鉛質粒子に残存し易くなり、いずれの場合も充放電容量が低下する傾向にある。

【００１９】次に得られた黒鉛化物を粉砕する。黒鉛化物の粉砕方法については特に制限を設けないが、ジェットミル、振動ミル、ピンミル、ハンマーミル等の既知の方法及びこれらの複数を組み合わせて用いることができる。粉砕後の粒子径は１００μm以下が好ましく、５０μm以下が更に好ましい。平均粒子径は大きすぎる場合、作製した電極表面に凹凸が出来やすくなる。更に、２種以上の細孔容積の異なる黒鉛質粒子で構成される負極を作製する場合、組み合わせる黒鉛質粒子の粒子径に対応して平均粒子径を設定しても良い。

【００２０】得られた黒鉛質粒子はそのまま２種以上のカサの異なる黒鉛質粒子からなる負極用炭素質材として使用可能であるが、更に非酸化性雰囲気中で、４００℃以上の温度で加熱処理しても良い。この処理により比表面積を３m^2／g以下に低下させることができ、リチウム二次電池の安全性及び不可逆容量が改善される。非酸化性雰囲気としては、例えば窒素雰囲気、アルゴン雰囲気、真空等が挙げられる。

【００２１】本発明のカサ比重が異なる２種以上の黒鉛質粒子を含むことを特徴とするリチウム二次電池の負極に用いられる黒鉛質粒子の内、カサ比重が０．８５～１．３０の範囲の黒鉛質粒子は、少なくとも黒鉛化可能な骨材又は黒鉛と黒鉛化可能なバインダを混合する工程、該混合物を５００～２０００℃で焼成する工程、該焼成物を平均粒径１０～１００μmに粉砕する工程、該粉砕物を２５００℃以上で黒鉛化する工程を有する製造方法によって製造されることが好ましい。

【００２２】黒鉛化可能な骨材と黒鉛化可能なバインダを、混合することで、得られる炭素粉末のアスペクト比を小さくすることができ、且つ偏平状の粒子を複数集合又は結合させた黒鉛質粒子を作製することが可能になる。その結果作製するリチウム二次電池の急速充放電特性及びサイクル特性を向上させることができる。黒鉛化可能な骨材としては、例えばコークス粉末、樹脂炭化物粉、黒鉛粉等が挙げられ、充放電容量及び急速充放電特性の点で、コークス粉末を含んでなることが好ましく、ニードルコークス粉を含んでなればより好ましい。また、骨材は、平均粒径が１～８０μmの粉末が好ましく、１～６０μmであればより好ましく、５～４０μmであれば更に好ましい。

【００２３】黒鉛化可能なバインダとしては、ピッチ、タールの他、熱硬化性樹脂、熱可塑性樹脂等の有機系材料が挙げられる。黒鉛化可能なバインダの添加量としては、使用するバインダの残炭率及び結着力によって異なるが、例えばピッチを使用した場合、黒鉛化可能な骨材１００重量部に対して１０～１００重量部が好ましく、１０～７０重量部であればより好ましく、１０～５０重量部であれば更に好ましい。

【００２４】また、黒鉛化可能な骨材と黒鉛化可能なバインダを混合する際に、黒鉛化触媒を添加しても良い。黒鉛化触媒を添加することで得られる黒鉛質粒子の結晶が発達しやすくなり得られるリチウム二次電池の放電容量を向上させることができる。黒鉛化触媒としては、Ｔｉ、Ｓｉ、Ｆｅ、Ｎｉ、Ｂ等の金属又は酸化物又は炭化物が好ましい。黒鉛化触媒は、骨材とバインダを混合する際に添加し、同時に混合することが好ましい。黒鉛化触媒の添加量は０～１０重量％以下が好ましく、０～５重量％以下であればより好ましい。黒鉛化触媒の添加量が増えると、放電容量が増加させることができる反面、比表面積が大きく且つかさ密度が低下する問題がある。

【００２５】混合する温度は、黒鉛化可能なバインダが軟化溶融する温度であることが好ましく、その温度は使用する材料によって異なるが、５０～３５０℃の範囲が好ましい。また黒鉛化可能なバインダを溶剤等によって、溶液にする場合には常温で混合しても良い。黒鉛化可能なバインダとしては、ピッチ、タール等の他、熱硬化性樹脂、熱可塑性樹脂等の有機系材料が挙げられる。

【００２６】次いで黒鉛化可能な骨材と黒鉛化可能なバインダを混合した混合物は、５００～２０００℃で焼成し、更に該焼成物を粉砕し、平均粒径を１０～１００μmに調整し、更に該粉砕物を２５００℃以上の温度で黒鉛化することが好ましい。

【００２７】粉砕前の焼成温度は５００～１５００℃が好ましく、７００～１５００℃であればより好ましい。粉砕前の焼成温度が２０００℃を超えると、得られる黒鉛質粒子のかさ密度が低く、かつ比表面積が大きく、かつアスペクト比が大きくなる問題がある。また粉砕前の

焼成温度が５００℃未満では、添加した黒鉛化可能なバインダの炭素化が不十分となりやすく、その結果、粉砕・黒鉛化後に粒子同士が結合してしまう問題がある。

【００２８】粉砕の方法としては特に制限はなく、例えば、ジェットミル、ハンマーミル、ピンミル等の衝撃粉砕方式をとることができる。本発明では、黒鉛化前に粉砕し粒度を調整し、黒鉛化後には粉砕を行わない方が、比表面積、かさ密度、アスペクト比の点で好ましい。

【００２９】黒鉛化の方法は特に制限はないが、例えば、自己揮発性ガス雰囲気、窒素雰囲気、アルゴン雰囲気、真空中等で２５００℃以上の温度で行うことが得られる黒鉛質粒子の結晶性及び放電容量の点で好ましい。黒鉛化温度は、２７００℃以上であればより好ましく、２９００℃であれば更に好ましく、３０００℃以上であれば特に好ましい。黒鉛化温度の上限としては３２００℃以下であることが好ましい。

【００３０】次に、本発明のリチウム二次電池の製造方法について説明する。カサ比重が異なる２種以上の黒鉛質粒子と、黒鉛質粒子同士を結着するための有機系結着剤とを均一に混合した後加圧形成するか、或は有機溶媒等を用いてペースト化して集電体上に塗布乾燥プレスするなど、公知の方法で負極を製作することが出来る。有機系結着剤としては、例えばポリエチレン、ポリプロピレン、エチレンプロピレンポリマー、ブタジエンゴム、スチレンブタジエンゴム、イオン導電性の大きな高分子化合物が使用できる。イオン導電性高分子化合物としては、ポリフッ化ビニリデン、ポリエチレンオキサイド、ポリエピクロヒドリン、ポリフォファゼン、ポリアクロニトリル等が使用できる。有機系結着剤の含有量は、黒鉛質粒子と有機系結着剤との混合物に対して３～２０重量％とすることが好ましい。

【００３１】本発明のカサ比重が異なる２種以上の黒鉛質粒子からなるリチウム二次電池用負極は、充放電可能なリチウムを含有する活物質から構成した正極と組み合わせてリチウム二次電池を構成する。ここで使用される正極活物質としては、$Li_xM_yO_z$（ここでＭ＝Ｖ、Ｍｎ、Ｆｅ、Ｃｏ、Ｎｉから選ばれる少なくとも一種の金属、ｘ＝０．０５～１．２、ｙ＝１或いは２、ｚ＝１．５～５）で表わされるリチウムを含有する遷移金属酸化物である。またこれらに、リチウム以外のアルカリ金属、アルカリ土類金属、上記Ｍ以外の遷移金属、あるいは周期律表１３～１５族元素（Ａｌ、Ｇａ、Ｉｎ、Ｓｉ、Ｇｅ、Ｓｎ、Ｐｂ、Ｓｂ、Ｂｉ、Ｐ、Ｂ）などを含んでいても良い。また、正極にはさらに活物質としてMnO_2、MnO_3、V_2O_5、TiO_2、TiS_2、ＦｅＳ、活性炭などの無機化合物やポリアニリンなどの高分子化合物等を選ぶこともできる。この場合には、予め、負極に所定量のリチウムを吸蔵させるか、又は所定量のリチウムを圧着させて使用することもできる。

【００３２】本発明のカサ比重が異なる２種以上の黒鉛質粒子からなる負極を備えたリチウム二次電池に用いられる非水系電解液としては、リチウム塩を高誘電率の有機溶媒に溶解させた溶液が好ましい。リチウム塩については特に制限はなく、$LiClO_4$、$LiPF_6$、$LiBF_4$、$LiCF_3SO_3$、等を使用することができる。また、有機溶媒は、リチウム塩を溶解して電気化学的に安定性を与え、かつ構成する負極・正極材に対して電気化学的に安定性を有するものであればよい。例えばエチレンカーボネート、プロピレンカーボネート、ジメチルカーボネート、ジエチルカーボネート、１，２－ジメトキシエタン、テトラヒドロフラン、アセトニトリル、スルホラン、γ－ブチロラクトン等、及びこれらの混合物が用いられる。

【００３３】本発明のカサ比重が異なる２種以上の黒鉛質粒子からなる負極を備えたリチウム二次電池においては、正極と負極と非水系電解液の他に、両極の接触を防止し、かつ電解液を保持し、リチウムイオンを通過できる機能を有するセパレータと、電極材を保持して集電する機能を有する集電体とを組み合わせて用いることが好ましい。セパレータとしては、例えばポリエチレン、ポリプロピレン又はポリテトラフルオロエチレン等の多孔質フィルムや不織布、織布等が挙げられる。セパレータの厚さは２０～２００μｍ程度が好ましい。また、集電体としては、正極・負極の活物質に対して電気化学的に安定性を有する導体を使用することができる。例えば、ニッケル、チタン、ステンレス、銅、アルミニウムが挙げられる。また、本発明の水銀圧入法で測定される０．０１～１００μｍの範囲の細孔容積が異なる２種以上の黒鉛質粒子からなる負極を備えたリチウム二次電池は、円筒型、箱型、コイン型、ボタン型、ペーパー型、カード型など、様々な形状とすることができる。

【００３４】偏平な粒子は複数、互いに非平行に集合或いは結合した黒鉛質粒子で、０．４～０．６５の範囲にカサ比重を有する黒鉛質粒子は、粒子の過剰な変形がない状態では、優れた急速充放電特性及びサイクル特性を有するが、負極作製条件に起因して粒子の過剰な変形が生じた場合、偏平な粒子は集電体面に平行に配向し易く、また粒子内及び粒子間の空隙も減少するため、リチウムイオンのドープ、脱ドープが起こりづらくなり、急速充放電特性及びサイクル特性が低下する。上記黒鉛質粒子に０．８５～１．３０の範囲のカサ比重を有する黒鉛質粒子を添加すると、該黒鉛質粒子は比較的緻密質であるため、上記黒鉛質粒子の過剰な変形を抑制し、その結果として急速充放電特性及びサイクル特性が改善される。また、該黒鉛質粒子は、それ自身が高い充放電容量を有し、また粒子内に細孔を有しているため急速充放電特性が比較的良好であり、更に形状、真密度などの特性についても上記黒鉛質粒子と類似しているため、均一な混合が容易に実現できるため、高い充放電容量のリチウム二次電池を安定して作製することが可能である。

【0035】
【実施例】以下、本発明の実施例及びその比較例を示して、その効果を具体的に説明するが、本発明は下記の実施例に制限されるものではない。
【0036】実施例1
（リチウム二次電池の作製）図1は円筒型リチウム二次電池の一部断面正面図を示し、7は正極、8は負極、9はセパレータ、10は正極タブ、11は負極タブ、12は正極蓋、13は電池缶及び14はガスケットである。図1に示すリチウム二次電池は以下のようにして作製した。
【0037】（正極の作製）正極活物質としての$LiCoO_2$88重量部に、導電剤として平均粒子径が1μmの鱗片状天然黒鉛7重量部と、結着剤としてのポリフッ化ビニリデン5重量部添加し、これにN－メチル－2－ピロリドンを加え混合して正極合剤のスラリーを調製した。次いで、この正極合剤を正極集電体としてのアルミニウム箔（厚さ25μm）にドクターブレード法により両面に塗布、乾燥し、次いでローラープレスによって電極を加圧成形した。幅40mmで長さが285mmの大きさに切り出して正極7を作製した。ただし、正極7の両端の長さ10mmの部分は正極合剤が塗布されておらずアルミニウム箔が露出しており、この一方に正極タブ10を超音波結合によって圧着した。
【0038】（黒鉛質粒子の作製）
（1）平均粒径が5μmのコークス粉末100重量部、タールピッチ40重量部、平均粒子径が48μmの炭化珪素14重量部及びコールタール20重量部を混合し、200℃で1時間混合した。得られた混合物を粉砕し、ペレット状に加圧成形し、次いで窒素雰囲気中、900℃まで加熱、次いでアチソン炉を用いて3000℃まで昇温し黒鉛化を行った。得られた黒鉛化物をハンマーミルを用いて粉砕、目開き200メッシュの篩を通し、平均粒径が20μmの黒鉛質粒子を作製した。この黒鉛質粒子のカサ比重は0．56であった。またBET法による比表面積は3．6m^2／gであった。得られた黒鉛質粒子について水銀圧入法による細孔径分布測定を行った結果、0．01～100μmの範囲に細孔を有し、全細孔体積は0．9cc／gであった。また、得られた黒鉛質粒子を100個任意に選び出し、アスペクト比を測定した結果、2．0であり、黒鉛質粒子のX線広角回折による結晶の層間距離d（002）は0．336nm及び結晶子の大きさLc（002）は100nm以上であった。更に、得られた黒鉛質粒子の走査型電子顕微鏡（SEM）写真によれば、この黒鉛質粒子は、偏平状の粒子が複数配向面が非平行となるように集合又は結合した構造をしていた。以上のようにして作製した黒鉛質粒子を以下A試料を称する。
【0039】（2）平均粒径20μmのニードルコークス粉末100重量部と、タールピッチ10重量部と、コールタール20重量部を230℃で1時間混合した。次いで、この混合物を窒素中1000℃で焼成した後、粉砕し、平均粒径38μmの粉末を作製した。この粉末をさらにアチソン炉を用いて3000℃で黒鉛化した後、目開き200メッシュの篩を通し、黒鉛質粒子を得た。得られた黒鉛質粒子を100個任意に選び出し、アスペクト比を測定した結果、2．5であり、黒鉛質粒子の、黒鉛質粒子のX線広角回折による結晶の層間距離d（002）は0．336nm及び結晶子の大きさLc（002）は100nm以上であった。更に、得られた黒鉛質粒子の走査型電子顕微鏡（SEM）写真によれば、この黒鉛質粒子は、偏平状の粒子が複数配向面が非平行となるように集合又は結合した構造をしていた。以上のようにして作製した黒鉛質粒子を以下B試料を称する。
【0040】（黒鉛質粒子の放電容量の測定）黒鉛質粒子90重量%に、N－メチル－2－ピロリドンに溶解したポリフッ化ビニリデン（PVDF）を固形分で10重量%加えて混練して黒鉛ペーストを作製した。この黒鉛ペーストを厚さ10μmの圧延銅箔に塗布し、更に乾燥し負極とした。
【0041】作製した試料電極を3端子法による定電流充放電を行い、リチウム二次電池用負極としての評価を行った。図2は実験に用いたリチウム二次電池の概略図である。ガラスセル1に電解液2として$LiPF_6$をエチレンカーボネート（EC）及びジメチルカーボネート（DMC）（EC：DMC＝1：1（体積比））の混合溶媒に1モル／lの濃度となるように溶解した溶液を入れ、試料電極3、セパレータ4及び対極5を積層して配置し、更に参照電極6を上部から吊るした。対極5及び参照電極6には金属リチウムを使用し、セパレータ4にはポリエチレン微孔膜を使用した。0．5mA／cm^2の定電流で、5mV（V vs Li／Li^+）まで充電し、1V（V vs Li／Li^+）まで放電する試験を行った。得られた結果を表1に示す。
【0042】
【表1】

試料	A試料	B試料
放電容量（mAh／g）	350 (100)	340 (97)
不可逆容量（mAh／g）	35	25

（　）：A試料の値を100％としたときの値

（負極の作製）A試料90重量部とB試料10重量部とを均一に混合し、次いでこの混合黒鉛と結着剤としてのPVDFとを、重量比90：10の比率で混合し、これを溶剤（N－メチル－2－ピロリドン）に分散させてスラリーとした後、負極集電体としての銅箔（厚さ10μm）の両面にドクターブレード法により塗布し、乾燥、次いでローラープレスによって電極を加圧成形して負極とした。幅40mmで長さが290mmの大きさに切り

出して負極８を作製した。この負極を正極と同様に、両端の長さ１０ｍｍの負極合剤が塗布されていない部分の一方に負極タブ１１を超音波接合によって圧着した。

【００４３】（電解液の調製）エチレンカーボネートとジメチルカーボネートとの等体積混合溶媒に、$LiPF_6$を１モル／ｌ溶解し、電解液を調製した。

【００４４】（電池の作製）前記正極７、ポリエチレン製多孔質フィルム（厚さ２５μｍ、幅４４ｍｍ）からなるセパレータ９及び前記負極８をそれぞれこの順序で積層した後、前記負極が外側に位置するように渦巻き状に捲回して電極群を作製した。この電極群をステンレス製の電池缶１３にそれぞれ収納し、負極タブ１１を缶底溶接し、正極蓋１２をかしめるための絞り部を設けた。この後、前記電解液を電池缶１３に注入した後、正極タブ１０を正極蓋１２に溶接し、正極蓋１２をかしめて円筒型リチウム二次電池を組み立てた。

【００４５】実施例２

負極作製でのＡ試料及びＢ試料の配合比をそれぞれ、８０重量部、２０重量部とした以外は実施例１と同様にして円筒型リチウム二次電池を組み立てた。

【００４６】実施例３

負極作製でのＡ試料及びＢ試料の配合比をそれぞれ、７０重量部、３０重量部とした以外は実施例１と同様にして円筒型リチウム二次電池を組み立てた。

【００４７】実施例４

負極作製でのＡ試料及びＢ試料の配合比をそれぞれ、６０重量部、４０重量部とした以外は実施例１と同様にして円筒型リチウム二次電池を組み立てた。

【００４８】実施例５

負極作製でのＡ試料及びＢ試料の配合比をそれぞれ、５０重量部、５０重量部とした以外は実施例１と同様にして円筒型リチウム二次電池を組み立てた。

【００４９】比較例１

負極作製でのＡ試料及びＢ試料の配合比をそれぞれ、１００重量部、０重量部とした以外は実施例１と同様にして円筒型リチウム二次電池を組み立てた。

【００５０】比較例２

負極作製でのＡ試料及びＢ試料の配合比をそれぞれ、０重量部、１００重量部とした以外は実施例１と同様にして円筒型リチウム二次電池を組み立てた。

【００５１】比較例３

負極作製において、Ａ試料の代わりに平均粒子径が２０μｍの鱗片状人造黒鉛粉を用い、配合比を該人造黒鉛粉７０重量部、Ｂ試料３０重量部とし、以下、実施例１と同様にして円筒型リチウム二次電池を作製した。該人造黒鉛粉のカサ比重は０．２４であり、単独で測定された放電容量、不可逆容量はそれぞれ、３４０ｍＡｈ／ｇ（対Ｂ試料比：１０１％）、８５ｍＡｈ／ｇであった。

【００５２】比較例４

平均粒径２０μｍのニードルコークス粉末１００重量部と、ピッチ１０重量部と、コールタール２０重量部を２３０℃で１時間混合した。次いで、この混合物を粉砕、成形した後、窒素中１０００℃で焼成、さらにアチソン炉を用いて３０００℃で黒鉛化した。得られた黒鉛成形体を粉砕し、目開き２００メッシュの篩を通し、黒鉛質粒子を得た。得られた黒鉛質粒子のかさ密度、平均粒径、比表面積、ｄ（００２）、Ｌｃ（００２）、アスペクト比は、それぞれ、０．３３６ｎｍ、１００ｎｍ以上、２．３であった。得られた黒鉛質粒子を電子顕微鏡で観察した結果、偏平状の粒子が複数集合又は結合した塊状の構造をしていた。また、この黒鉛質粒子の単独で測定された放電容量、不可逆容量はそれぞれ、３４３ｍＡｈ／ｇ、２０ｍＡｈ／ｇであった。この黒鉛質粒子３０重量部、Ａ試料７０重量部として負極を作製し、以下、実施例１と同様にして円筒型リチウム二次電池を作製した。

【００５３】比較例５

メソフェーズピッチを平均粒径３２μｍに粉砕した後、３００℃で酸化処理をした後、窒素中、１０００℃で焼成した。次いで、この粉末をアチソン炉を用いて３０００℃で黒鉛化後、目開き２００メッシュの篩を通し、黒鉛質粒子を得た。得られた黒鉛質粒子のかさ密度、平均粒径、比表面積、ｄ（００２）、Ｌｃ（００２）、アスペクト比は、それぞれ、０．３３６ｎｍ、１００ｎｍ以上、１．８であった。得られた黒鉛質粒子を電子顕微鏡で観察した結果、塊状の粒子形状をしていた。また、この黒鉛質粒子の単独で測定された放電容量、不可逆容量はそれぞれ、３３０ｍＡｈ／ｇ、１８ｍＡｈ／ｇであった。この黒鉛質粒子３０重量部、Ａ試料７０重量部として負極を作製し、以下、実施例１と同様にして円筒型リチウム二次電池を作製した。

【００５４】得られた実施例１～５及び比較例１～５のリチウム二次電池について、充電終止電圧を４．１５Ｖ、放電終止電圧を２．８Ｖとし、充放電電流を２００ｍＡから８００ｍＡの範囲で変化させ、急速充放電時の放電容量を測定した。その結果を比較例１の充放電電流２００ｍＡの時の放電容量を１００％として図３に示す。また、充放電電流２００ｍＡとして各電池の充放電サイクル特性を測定した。その結果を比較例１のサイクル数１の時の放電容量を１００％として図４に示す。

【００５５】図３より明らかなように、実施例の急速充放電特性は比較例と比較して良好であり、大きな充放電電流においても放電容量の低下が極めて少ないことが分かる。また、図４より明らかなように、実施例のサイクル特性は、比較例と比較して良好であり、高いサイクル数を経ても大きな放電容量を維持できることが分かる。

【００５６】

【発明の効果】以上で説明したように、本発明によれば、特に高い充放電電流で充放電を行った場合のリチウムの吸蔵・放出量が多くて充放電容量が大きく、かつ充

放電サイクルによる充放電容量の低下が少ないリチウム二次電池を得ることができる。

【図面の簡単な説明】

【図１】円筒型リチウム二次電池の一部断面正面図である。

【図２】実験に用いたリチウム二次電池の概略図である。

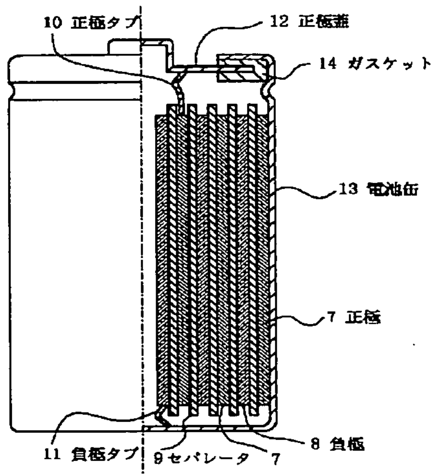
【図３】実施例１～５及び比較例１～５のリチウム二次電池の急速充放電試験における充放電電流と放電容量との関係を示すグラフである。

【図４】実施例１～５及び比較例１～５のリチウム二次電池のサイクル試験におけるサイクル数と放電容量との関係を示すグラフである。

【符号の説明】

１　ガラスセル
２　電解液
３　試料電極
４　セパレータ
５　対極
６　参照極
７　正極
８　負極
９　セパレータ
１０　正極タブ
１１　負極タブ
１２　正極蓋
１３　電池缶
１４　ガスケット

【図１】



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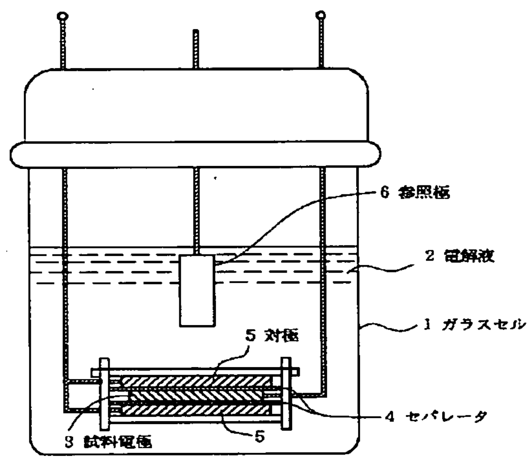

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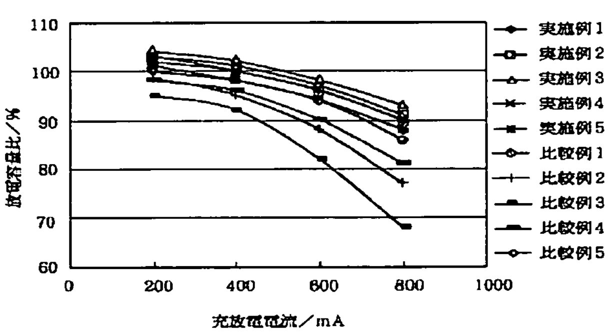

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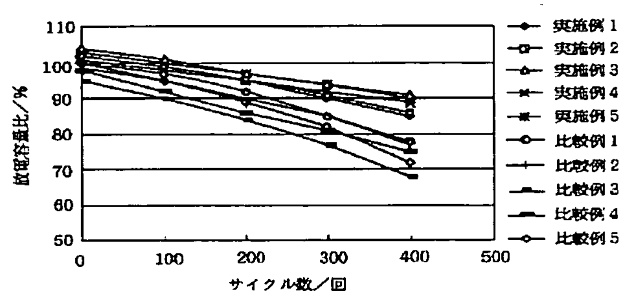

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(54) LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a lithium secondary battery available at a low cost and having high lithium occulusion and emission, high charge and discharge capacity, and a low decrease in charging and discharging capacity in a charging and discharging cycle when charged and discharged particularly with large charging and discharging current.

SOLUTION: In the lithium secondary battery having a negative electrode consisting of a carbonaceous material occuluding and emitting a lithium ion, a positive electrode, and a nonaqueous electrolytic solution, the carbonaceous material uses a carbonaceous material containing two kinds of more of graphite particles having different bulk specific gravity.

CLAIMS

[Claim(s)]

[Claim 1] The lithium secondary battery characterized by said carbonaceous object containing two or more sorts of graphite particles from which bulk specific gravity differs in the negative electrode and positive electrode which consist a lithium ion of occlusion and a carbonaceous object to emit, and the lithium secondary battery which has nonaqueous electrolyte.

[Claim 2] The lithium secondary battery according to claim 1 with which a carbonaceous object consists of a graphite particle which has bulk specific gravity in the range of 0.4-0.65, and a graphite particle which has bulk specific gravity in the range of 0.85-1.30.

[Claim 3] The lithium secondary battery according to claim 2 whose bulk specific gravity is the range of 0.85-1.30 and whose distance d(002) between layers of the crystal of the graphite particle 0.338nm or less and the microcrystal size Lc of C shaft orientations (002) is 50nm or more and mean particle diameter is 10-100 micrometers and specific surface area is 0.3-2.0m^2/g and the structure of this graphite particle of an aspect ratio of the range is 1.1-5 , and two or more of the graphite particle which gather, or joins together, and becomes about a flat-like particle.

[Claim 4] The lithium secondary battery according to claim 2 which is the graphite particle manufactured by the manufacturing method in which bulk specific gravity has the process at which the graphite particle of the range of 0.85-1.30 graphitizes the process which mixes the aggregate and the binder which can be graphitized which can be graphitized at least, the process which calcinates this mixture at 500-2000 ℃, the process which grinds this baking object in mean particle diameter of 10-100 micrometers, and this grinding object above 2500 ℃.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to the lithium secondary battery excellent in charge-and-discharge capacity, the rapid charge-and-discharge property, and the cycle property about a lithium secondary battery.

[0002]

[Description of the Prior Art] In recent years, small and the requests to the rechargeable battery which is lightweight and has a high energy consistency are mounting as a portable device, an electric vehicle, and an object for stationary energy storage. The nonaqueous electolyte rechargeable battery, especially the lithium secondary battery attract attention to such a request as cells which especially have a high voltage and a high energy consistency.

[0003] As a negative-electrode ingredient of a lithium secondary battery, the metal lithium, the low graphitized-carbon particle, and the high graphitized-carbon particle are used. Although a metal lithium can realize high charge-and-discharge capacity, for [the] high reactivity, with progress of a charge-and-discharge cycle, it reacts with the solvent in the electrolytic solution, and capacity falls. Moreover, it is easy to generate the metal lithium of arborescence, and the separator formed between forward and a negative electrode is penetrated, and it has the trouble of being easy to cause a short circuit. Although an arborescence metal lithium with low reactivity with the electrolytic solution generates the nature ingredient of low graphitized carbon and it has the description of ******, it is not attained that charge-and-discharge capacity has low the difficulty that the charge-and-discharge capacity per volume is low since true density is low, and it generally realizes the rechargeable battery of a high energy consistency. On the other hand, since a high graphitized-carbon particle has a high charge-and-discharge capacity as compared with a low graphitized-carbon particle, reactivity with the electrolytic solution and an arborescence metal lithium generate it as compared with a metal lithium and it has the description of ******, examination is briskly made increasingly as a charge of negative-electrode material in recent years.

[0004] The nature particle of an artificial graphite manufactured by carbonizing and graphitizing the natural graphite base particle and corks which were high-grade-ized, a pitch, or synthetic organic polymeric materials as a high graphitized-carbon particle is used. By these nature particles of high graphitized carbon, since the graphite crystal has developed into altitude, the configuration is carrying out the shape of a big scale of an aspect ratio. For this reason, when it kneaded with the binder, it applied to the charge collector and an electrode is produced, A scale-like graphite particle carries out orientation to high density in the direction of a field of a charge collector. The result, The permeability of the electrolytic solution into a negative-electrode

layer gets worse, and since a particle tends to exfoliate by distortion of the thickness direction which charge-and-discharge capacity generates by the repeat of the occlusion and emission of the lithium to the graphite particle to which a fall and a high-speed charge-and-discharge property fall, problems, like a cycle property is bad occur. On the other hand, in order to avoid the above problems, if the consistency of the graphite particle in an electrode is reduced, the problem that the charge-and-discharge capacity per volume falls will occur.

[0005] The improvement of the property of a high graphitization particle is tried as the technique of solving such a problem. on the JP,2637305,B specifications, the mesophase microsphere extracted from the mesophase pitch was graphitized, and it was obtained -- spherical -- the orientation of a detailed organization -- a radial or the graphitization particle of a Brooks-Taylor mold -- And although it has proposed that the orientation of a detailed organization uses the carbon fiber of a lamellae mold or a Brooks-Taylor mold Since charge-and-discharge capacity of the former is comparatively as low as 280 - 300 mAh/g and the process of the extract from a mesophase pitch and separation is required for it, it is quantity cost, and the densification of an electrode will penetrate a separator, if difficulty and continuous glass fiber are intermingled, and the latter has the problem that a short circuit tends to take place. Although the particle to which the graphite microcrystal ground and manufactured carried out orientation of the high density graphite Plastic solid produced considering the aggregate and binding material as a start raw material to JP,7-335216,A at random is proposed, the manufacture approach of the Plastic solid using a cold-isostatic-pressing method is lacking in productivity. As an approach of pulverizing the graphitized Plastic solid and obtaining a graphite particle, the approach indicated by the re-official announcement patent WO 95/No. 28011 official report and JP,9-231974,A in addition to this is mentioned. Bulk density is high intensity highly, and since the graphite crystal is carrying out orientation of each graphite powder which pulverizes these graphitization Plastic solids and is obtained at random within the particle, it is an effective means at the point that the opening between the particles which the orientation of the graphite crystal on a charge collector is controlled, and the electrolytic solution can permeate is secured. However, that a particle is high bulk specific gravity, i.e., the substantia compacta, controls osmosis of the electrolytic solution into a particle shortly, and it has become the cause of making improvement in a rapid charge-and-discharge property producing a limitation. As an approach of solving this problem, artificers set to JP,10-158005,A etc., are the graphite particles which the flat-like graphite particle gathered or combined with two or more each other being un-parallel, and proposed the graphite particle which has the pore of 0.4 - 2.0 cc/g in the range of 0.1-100 micrometers. Although such a graphite particle shows the extremely excellent rapid charge-and-discharge property since osmosis of the electrolytic solution inside [which was the technical problem of a graphite particle whenever / upper high bulk density] a particle is realized, there is a problem on which a charge-and-discharge cycle property deteriorates that that it is a low bulk density particle tends to generate deformation of a graphite particle and the orientation as the result depending on an electrode process condition shortly, and the working condition of negative-electrode production was limited.

[0006] The technique which mixes and uses a high graphitized-carbon particle and other ingredients is proposed. Although preventing exfoliation of the particle by the repeat of charge and discharge by combining a spherical graphite carbon particle and a spherical carbon fiber is proposed in JP,4-237971,A, reference is not made about the high graphitized-carbon particle except spherical. Although preventing the rapid voltage drop of the discharge last stage, and

making the terminal point judging of cell capacity easy by using the mixture of a high graphitized-carbon particle and a low graphitized-carbon particle is proposed in JP,6-36760,A Since reference is not made about the orientation to the direction of current collection dignity of a high graphitization particle, and discharge voltage falls when there are many additions of a low graphitized-carbon particle, the upper limit 30 capacity % is prepared in the addition. Although [JP,6-111818,A] have proposed combining a nodular graphite carbonizing elementary particle and a graphitized-carbon staple fiber, electrode reinforcement is made to increase and an improvement of the rapid charge-and-discharge property by control of destruction of the electrode layer accompanying a charge-and-discharge cycle and the conductive improvement in the electrode layer by the staple fiber can be aimed at Since the reference about high graphitized-carbon particles other than a nodular graphite carbonizing elementary particle is not made, and an electrode consistency falls when there are many additions of a graphitized-carbon staple fiber, and the charge-and-discharge capacity per volume falls, the upper limit 30 capacity % is prepared in the addition of a graphitized-carbon staple fiber. Although high-intensity-izing an electrode and preventing exfoliation of a particle by combining an inactive metallic-coating whisker with the nature particle of nodular graphite chemically and electrochemically is proposed in JP,6-302315,A, in order for there to be no reference about the graphite particle except spherical and not to contribute to charge and discharge at the whisker to add, when there are many additions, it is in ** that the fall of charge-and-discharge capacity occurs. By adding the nature particle of nodular graphite, the nature particle of non-nodular graphite which has the mean particle diameter of the ratio of 1.3-4.0 to the mean particle diameter of this spherical particle, and a carbon fiber grinding object to JP,8-180864,A, there is a publication of the purport by which the electronic conduction nature in an electrode improves and a charge-and-discharge cycle property is improved. It is mentioned that a non-spherical particle (an artificial graphite, natural graphite) turns to various directions, and exists between the nature particles of nodular graphite in this. Although it is shown that existence of the nature particle of nodular graphite has effectiveness [controlling the orientation to the direction of current collection dignity of the above-mentioned scale-like graphite particle], it is necessary to control the particle diameter of a spherical particle and a non-spherical particle to a precision, and there is a problem in respect of productivity. There is a publication of the purport in which it is high-density and a graphite crystal carries out orientation in the direction of current collection dignity and by which exfoliation of the particle from the charge collector accompanying ****** and charge-and-discharge cycle progress is controlled by adding the carbon fiber powder graphitized to the letter of a block, the shape of a flake, the granular artificial graphite, or the natural graphite base particle to JP,8-83608,A and JP,8-83609,A. However, the graphitized-carbon fiber powder addition of this effectiveness being acquired is to 20 % of the weight, and it is mentioned more than by this that the electrode engine performance falls.

[0007] since particle shape differ greatly when it especially have the problem , respectively and combine with graphitized carbon fiber in the mixed stock of the nature particle of high graphitized carbon showed above , and other ingredients , there be a common problem that it be difficult to mix to homogeneity and manufacture of the lithium secondary battery which the part beyond the upper limit of the addition which be show in each patent public presentation official report for this reason might generated , and be stabilized be difficult . Moreover, as the system containing the nature particle of nodular graphite which graphitized the mesophase microsphere and was obtained was described in the top, the charge-and-discharge capacity of this nature

particle of nodular graphite is comparatively low, and it has the trouble of being high cost.
[0008]
[Problem(s) to be Solved by the Invention] The purpose of this invention has many occlusion and burst sizes of the lithium at the time of performing charge and discharge by the high charge and discharge current especially, and its charge-and-discharge capacity is large, and obtaining few lithium secondary batteries by low cost has the fall of the charge-and-discharge capacity by the charge-and-discharge cycle.
[0009]
[Means for Solving the Problem] This invention relates to the lithium secondary battery characterized by said carbonaceous object containing two or more graphite particles from which bulk specific gravity differs in the negative electrode and positive electrode which consist a lithium ion of occlusion and a carbonaceous object to emit, and the lithium secondary battery which has nonaqueous electrolyte.
[0010] This invention relates to said lithium secondary battery which consists of a graphite particle to which said carbonaceous object has bulk specific gravity in the range of 0.4-0.65, and a graphite particle which has bulk specific gravity in the range of 0.85-1.30 again.
[0011] The distance d(002) between layers of the crystal of the graphite particle is of the range of 0.338nm or less and, as for this invention, the microcrystal size Lc (002) of C shaft orientations is 50nm or more is related [said bulk specific gravity 0.85-1.30 / the distance and specific surface area 0.3-2.0m^2/g and an aspect ratio 1.1-5,] with said lithium secondary battery whose structure of this graphite particle is the graphite particle which gather, or joins together, and becomes about a flat-like particle by and mean particle diameter 10-100 micrometers again. [two or more]
[0012] This invention relates to said lithium secondary battery which is the graphite particle from which said bulk specific gravity was manufactured again by the manufacturing method which has the process at which the graphite particle of the range of 0.85-1.30 graphitizes the process which mixes the aggregate which can be graphitized at least, and the binder which can be graphitized, the process which calcinates this mixture at 500-2000 ℃, the process which grinds this baking object in mean particle diameter of 10-100 micrometers, and this grinding object above 2500 ℃.
[0013]
[Embodiment of the Invention] This invention is explained in full detail below.
[0014] The carbonaceous object for negative electrodes used by this invention consists of two or more graphite particles from which bulk specific gravity differs. The bulk specific gravity described here is JIS. It is the value measured by the approach indicated by K-1469. When the small graphite particle of one kind of bulk specific gravity is used, depending on the production conditions of an electrode, a particle deforms superfluously, it is easy to carry out orientation of the graphite crystal in the direction of a field of a charge collector, a cycle property and a rapid charge-and-discharge property deteriorate, and charge-and-discharge capacity tends to fall. On the other hand, when one kind of bulk specific gravity uses a large graphite particle, osmosis of the electrolytic solution into a particle is inadequate, and a rapid charge-and-discharge property falls. As for at least one, as a graphite particle which constitutes the carbonaceous ingredient for negative electrodes, it is desirable that the graphite particle which has bulk specific gravity in the range of 0.4-0.65 is included, and it is desirable to use together the graphite particle in the range of 0.4-0.65 and the graphite particle which has bulk specific gravity in the range of 0.85-1.30. when the bulk specific gravity of the former graphite particle is less than the minimum, there is an inclination for the viscosity of the slurry used for electrode production to become high, and it is

necessary to make [many] a binder addition -- etc. -- it is not desirable from a reason. On the other hand, when the bulk specific gravity of the former graphite particle exceeds the upper limit, there is an inclination for a rapid charge-and-discharge property to fall. When the bulk specific gravity of the latter graphite particle is less than the minimum, superfluous deformation of the graphite particle by electrode production conditions tends to take place, and there is an inclination for a cycle property and a rapid charge-and-discharge property to fall. When the latter bulk specific gravity exceeds the upper limit, there is an inclination for a rapid charge-and-discharge property to fall. About the compounding ratio of two or more graphite particles from which bulk specific gravity differs, it does not restrict especially by this invention, but although chosen to compensate for the design of a lithium secondary battery made into the purpose, the latter is preferably used for the former five to 60% of the weight 40 to 95% of the weight.

[0015] As for which lattice spacing d (002), microcrystal size Lc of C shaft orientations (002), and true density of a field (002) of two or more graphite particles from which the bulk specific gravity which constitutes a negative electrode differs, it is desirable respectively to consider as 0.338nm or less, 50nm or more, and three or more 2.21 g/cm. They may be 0.335-0.338nm and 60nm or more respectively more preferably. An almost equal thing is suitable for each charge-and-discharge capacity, it considers as 330 or more mAh/g more preferably, and 300 or more mAh/g of the difference between graphite particles is further made into 5% or less more preferably 10% or less. The effectiveness which combined two or more sorts of graphite particles from which bulk specific gravity differs, without accompanying this by change (fall) of charge-and-discharge capacity can be acquired. Moreover, as for the graphite particle of the range of 0.4-0.65, it is desirable to have pore in the range of 0.01-100 micrometers in which bulk specific gravity is measured with a method of mercury penetration, and the value has the desirable range of 0.4 cc/g-2.0cc/g. Moreover, an almost equal thing is suitable for the configuration of two or more graphite particles where the bulk specific gravity which constitutes a negative electrode differs, and aspect ratios are 1.1-5 preferably. When this constitutes a negative electrode combining two or more sorts of graphite particles from which bulk specific gravity differs, uniform distribution of these graphite particles is realized easily, and a good lithium secondary battery with little dispersion can be obtained. Furthermore, it is related with the specific surface area of two or more graphite particles from which the bulk specific gravity which constitutes a negative electrode differs. Bulk specific gravity is 2.0-5.0m^2/g by the graphite particle of the range of 0.4-0.65. It is desirable that bulk specific gravity considers as the range of 0.3-2.0m^2/g by the graphite particle of the range of 0.85-1.30 on the other hand. Change of the viscosity of the mixture of the graphite particle, binder, and solvent which are used in case it is not accompanied by the increment in irreversible capacity even if it produces a negative electrode combining two or more sorts of graphite particles from which bulk specific gravity differs by this, and a negative electrode is produced can be made into the minimum. Furthermore, it is desirable that it is the graphite particle which is related with the particulate structure of two or more sorts of graphite particles from which the bulk specific gravity which constitutes a negative electrode differs, gather, or joins together, and becomes about a flat-like particle. [two or more] In this invention, a flat-like particle is a particle of a configuration which has a major axis and a minor axis, and a perfect not spherical thing is said. For example, the thing of configurations, such as the shape of a lepidic form and a scale and massive [a part of], is contained in this. Although the condition that the particle with mutual association has joined together chemically through the carbon which

carbonized binders, such as tar and a pitch, is said although it set to this graphite particle and the flat-like particle is gathered or combined, and the mutual particle has not combined the set chemically, it originates in that configuration and the condition of maintaining the configuration as that aggregate is said. From the field of mechanical reinforcement, a united thing is desirable. Moreover, it is desirable that the graphite particle gathered or combined so that the orientation side of a flat-like particle may become un-parallel as a condition of the set of the particle of the shape of flat [of a graphite particle] or association is included. Here, the orientation side of a flat-like particle says the field and the condition of having gathered without the particle of the shape of flat [two or more] gathering each orientation side in the fixed direction by making the field nearest to [flat] and others into an orientation side if it puts in another way which carried out flat of having being un-parallel in the configuration of each particle.

[0016] By making structure of a graphite particle like [the above], it becomes possible to raise more the rapid charge-and-discharge property and cycle property of a lithium secondary battery to produce.

[0017] Among the graphite particles used for the negative electrode of the lithium secondary battery characterized by including two or more sorts of graphite particles from which the bulk specific gravity of this invention differs, it is ground and manufactured, after adding a graphitization catalyst one to 50% of the weight to the binder which bulk specific gravity graphitizes [the aggregate or the graphite which can graphitize the graphite particle of the range of 0.4-0.65, and], mixing and calcinating and graphitizing. As the aggregate which can be graphitized, various corks, such as fluid coke and needle coke, are usable. Moreover, the already graphitized aggregates, such as a natural graphite and an artificial graphite, may be used. As a binder which can be graphitized, a coal system, a petroleum system, the various pitches of artificial **, and tar are usable. As a graphitization catalyst, iron, nickel, titanium, boron, silicon, etc. have these oxides, carbide, an usable nitride, etc. A graphitization catalyst is added one to 50% of the weight to the aggregate or the graphite which can be graphitized, and the binder which can be graphitized. The compounding ratio of the aggregate which can be graphitized or a graphite, the binder which can be graphitized, and a graphitization catalyst is the graphite particle made into the purpose, especially is chosen according to pore volume. Furthermore, about a graphitization catalyst, development of the crystal of a graphite particle worsens that the addition is less than 1 % of the weight, and charge-and-discharge capacity falls. On the other hand, since it becomes difficult to mix to homogeneity if it exceeds 50 % of the weight and dispersion in aggravation of workability and the property of the graphite particle obtained becomes large, it is not desirable.

[0018] It graphitizes by adding a graphitization catalyst one to 50% of the weight to the aggregate which can be graphitized, or the binder which can be graphitized, mixing to it, and calcinating to it. Before baking, said mixture may be fabricated in a suitable form if needed. As for baking, it is desirable to carry out in the ambient atmosphere in which said mixture cannot oxidize easily, for example, the approach of calcinating in nitrogen-gas-atmosphere mind, argon gas, and a vacuum is mentioned. The temperature of graphitization has desirable 2000 ℃ or more, it is more desirable that it is 2500℃ or more, and it is still more desirable that it is 2800 ℃ or more. If graphitization temperature is low, while development of the crystal of a graphite will worsen, it becomes easy to remain to the graphite particle which the graphitization catalyst produced, and is in the inclination for charge-and-discharge capacity to fall in any case.

[0019] Next, the obtained graphitization object is ground. Although a limit is not prepared

especially about the grinding approach of a graphitization object, it can use combining known approaches and these plurality, such as a jet mill, a vibration mill, a pin mill, and a hammer mill. The particle diameter after grinding has desirable 100 micrometers or less, and its 50 micrometers or less are still more desirable. When too large, irregularity becomes easy to be made by mean particle diameter in the produced electrode surface. Furthermore, when producing the negative electrode which consists of graphite particles from which two or more sorts of pore volume differs, mean particle diameter may be set up corresponding to the particle diameter of the graphite particle to combine.

[0020] Although the obtained graphite particle is usable as carbonaceous material for negative electrodes which consists of a graphite particle from which two or more sorts of umbrellas differ as it is, you may heat-treat at the temperature of 400 ℃ or more in a non-oxidizing atmosphere further. Specific surface area can be reduced below to $3m^2/g$ by this processing, and the safety and irreversible capacity of a lithium secondary battery are improved. As a non-oxidizing atmosphere, nitrogen-gas-atmosphere mind, an argon ambient atmosphere, a vacuum, etc. are mentioned, for example.

[0021] The inside of the graphite particle used for the negative electrode of the lithium secondary battery characterized by including two or more sorts of graphite particles from which the bulk specific gravity of this invention differs, Bulk specific gravity the graphite particle of the range of 0.85-1.30 The process which mixes the binder which can be graphitized with the aggregate or the graphite which can be graphitized at least, It is desirable to be manufactured by the manufacture approach of having the process which calcinates this mixture at 500-2000 ℃, the process which grinds this baking object in mean particle diameter of 10-100 micrometers, and the process which graphitizes this grinding object above 2500 ℃.

[0022] It becomes possible to produce the graphite particle which the aspect ratio of the carbon powder obtained can be made small, and combined [combine together and more than one gathered / particle] the flat-like particle by mixing the aggregate and the binder which can be graphitized which can be graphitized. The rapid charge-and-discharge property and cycle property of a lithium secondary battery which are produced as a result can be raised. As the aggregate which can be graphitized, for example resinous coal ghost powder, graphite powder, etc. are mentioned in the end of a coke breeze, it is the point of charge-and-discharge capacity and a rapid charge-and-discharge property, and it is desirable to come to contain the end of a coke breeze, and if it comes to contain needle coke powder, it is more desirable. Moreover, the powder whose mean particle diameter is 1-80 micrometers is desirable, and the aggregate is more desirable if it is 1-60 micrometers, and if it is 5-40 micrometers, it is still more desirable.

[0023] As a binder which can be graphitized, organic system ingredients, such as thermosetting resin besides a pitch and tar and thermoplastics, are mentioned. When a pitch is used, for example, the 10 - 100 weight section is desirable to the aggregate 100 weight section which can be graphitized, if it is 10 - 70 weight section, it is more desirable, and although it changes with the actual carbon ratios and binding capacity of a binder to be used as an addition of the binder which can be graphitized, it is still more desirable if it is 10 - 50 weight section.

[0024] Moreover, a graphitization catalyst may be added in case the aggregate and the binder which can be graphitized which can be graphitized are mixed. The discharge capacity of the lithium secondary battery with which the crystal of the graphite particle obtained by adding a graphitization catalyst tends to progress, and can become can be raised. As a graphitization catalyst, a metal, an oxide, or carbide, such as Ti, Si, Fe, nickel, and B, is desirable. As for a

graphitization catalyst, it is desirable to add, in case a binder is mixed with the aggregate, and to mix to coincidence. Its 0 - 10 or less % of the weight is desirable, and if the addition of a graphitization catalyst is 0 - 5 or less % of the weight, it is more desirable. If the addition of a graphitization catalyst increases, while discharge capacity can make it increase, there is a problem to which specific surface area is large and bulk density falls.

[0025] As for the temperature to mix, it is desirable that it is the temperature in which the binder which can be graphitized carries out softening fusion, and although the temperature changes with ingredients to be used, the range of 50-350 ℃ is desirable. Moreover, with a solvent etc., when using as a solution the binder which can be graphitized, it may be mixed in ordinary temperature. As a binder which can be graphitized, organic system ingredients, such as thermosetting resin besides being a pitch, tar, etc. and thermoplastics, are mentioned.

[0026] Subsequently, as for the mixture which mixed the aggregate and the binder which can be graphitized which can be graphitized, it is desirable to calcinate at 500-2000 ℃, to grind this baking object further, to adjust mean particle diameter to 10-100 micrometers, and to graphitize this grinding object at the temperature of 2500 ℃or more further.

[0027] Its 500-1500 ℃ are desirable, and if the burning temperature before grinding is 700-1500 ℃, it is more desirable. When the burning temperature before grinding exceeds 2000 ℃, the bulk density of the graphite particle obtained is low, specific surface area is large, and there is a problem to which an aspect ratio becomes large. Moreover, there is a problem which it is easy to become insufficient [less than 500 ℃] carbonizing [of the added binder which can be graphitized] the burning temperature before grinding, consequently particles combine after grinding / graphitization.

[0028] There is especially no limit as the approach of grinding, for example, impact crushing methods, such as a jet mill, a hammer mill, and a pin mill, can be taken. It is more desirable to grind before graphitization, to adjust grain size and not to grind after graphitization in this invention, in respect of specific surface area, bulk density, and an aspect ratio.

[0029] Although especially a limit does not have the approach of graphitization, it is desirable to carry out at the temperature of 2500 ℃ or more for example, by the self-volatility gas ambient atmosphere, nitrogen-gas-atmosphere mind, the argon ambient atmosphere, and the vacuum middle class in respect of the crystallinity of the graphite particle obtained, and discharge capacity. Graphitization temperature is more desirable if it is 2700 ℃ or more, if it is 2900 ℃, it is still more desirable, and especially if it is 3000 ℃ or more, it is desirable. It is desirable that it is 3200 ℃ or less as an upper limit of graphitization temperature.

[0030] Next, the manufacture approach of the lithium secondary battery of this invention is explained. A negative electrode can be manufactured by well-known approaches, such as carrying out pressurization formation, or pasting using an organic solvent etc. and carrying out a spreading desiccation press on a charge collector, after mixing to homogeneity two or more sorts from which bulk specific gravity differs of graphite particles, and the organic system binder for binding graphite particles. As an organic system binder, polyethylene, polypropylene, an ethylene propylene polymer, butadiene rubber, styrene butadiene rubber, and the big high molecular compound of ion conductivity can be used, for example. As an ion conductive polymer compound, polyvinylidene fluoride, polyethylene oxide, the poly epichlorohydrin compounds, poly phosphazene, polyacrylonitrile, etc. can be used. As for the content of an organic system binder, it is desirable to consider as 3 - 20 % of the weight to the mixture of a graphite particle and an organic system binder.

[0031] The negative electrode for lithium secondary batteries which consists of two or more sorts of graphite particles from which the bulk specific gravity of this invention differs constitutes a lithium secondary battery combining the positive electrode constituted from an active material containing the lithium in which charge and discharge are possible. It is the transition-metals oxide which contains the lithium expressed with $Li_xM_yO_z$ (at least a kind of metal chosen from M=V, and Mn, Fe, Co and nickel here, x=0.05-1.2, y= 1 or 2, z=1.5-5) as positive active material used here. Moreover, alkali metal other than a lithium, alkaline earth metal, transition metals other than Above M, the periodic table 13 - 15 group element (aluminum, Ga, In, Si, germanium, Sn, Pb, Sb, Bi, P, B), etc. may be included in these. Moreover, high molecular compounds, such as inorganic compounds, such as MnO_2, MnO_3, V_2O_5, TiO_2, TiS_2 and FeS, and activated carbon, and the poly aniline, etc. can also be further chosen as a positive electrode as an active material. In this case, it can also be used, carrying out occlusion of the lithium of the specified quantity to a negative electrode, or making the lithium of the specified quantity stick by pressure beforehand.
[0032] As a nonaqueous electolyte used for the lithium secondary battery equipped with the negative electrode which consists of two or more sorts of graphite particles from which the bulk specific gravity of this invention differs, the solution made to dissolve lithium salt in the organic solvent of a high dielectric constant is desirable. There is especially no limit about lithium salt, and $LiClO_4$, $LiPF_6$, $LiBF_4$, $LiCF_3SO_3$, etc. can be used. Moreover, an organic solvent dissolves lithium salt and should just have stability electrochemically to the negative electrode and positive-electrode material which gives and constitutes stability electrochemically. For example, such mixture, such as ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, 1, 2-dimethoxyethane, a tetrahydrofuran, an acetonitrile, a sulfolane, and γ -butyrolactone, is used.
[0033] It is desirable to use combining the charge collector which has the separator which has the function in which the contact of two poles other than a positive electrode, a negative electrode, and a nonaqueous electolyte is prevented, and the electrolytic solution is held in the lithium secondary battery equipped with the negative electrode which consists of two or more sorts of graphite particles from which the bulk specific gravity of this invention differs, and a lithium ion can be passed, and the function which holds electrode material and collects a current. As a separator, porosity films and nonwoven fabrics, such as polyethylene, polypropylene, or polytetrafluoroethylene, textile fabrics, etc. are mentioned, for example. The thickness of a separator has desirable about 20-200 micrometers. Moreover, the conductor which has stability electrochemically to the active material of a positive electrode and a negative electrode as a charge collector can be used. For example, nickel, titanium, stainless steel, copper, and aluminum are mentioned. Moreover, the lithium secondary battery equipped with the negative electrode which consists of two or more sorts of graphite particles from which the pore volume of the range of 0.01-100 micrometers measured with the method of mercury penetration of this invention differs can be made into various configurations, such as cylindrical, a core box, a coin mold, a carbon button mold, a paper mold, and a card mold.
[0034] Although the graphite particle which flat particles are plurality and a graphite particle mutually gathered or combined with being un-parallel, and has bulk specific gravity in the range of 0.4-0.65 has the outstanding rapid charge-and-discharge property and the outstanding cycle property in the condition that there is no superfluous deformation of a particle When it originates in negative-electrode production conditions and superfluous deformation of a particle arises, in order that it may be easy to carry out orientation of the flat particle in parallel with current

collection dignity and the openings in a particle and between a particle may also decrease in number, the dope of a lithium ion and a dedope are hard coming to happen, and a rapid charge-and-discharge property and a cycle property fall. If the graphite particle which has the bulk specific gravity of the range of 0.85-1.30 to the above-mentioned graphite particle is added, since this graphite particle is the substantia compacta comparatively, superfluous deformation of the above-mentioned graphite particle will be controlled, and a rapid charge-and-discharge property and a cycle property will be improved as the result. Moreover, since this graphite particle has charge-and-discharge capacity with high itself and has pore in the particle, its rapid charge-and-discharge property is comparatively good, since it is further similar with the above-mentioned graphite particle also about properties, such as a configuration and true density, and uniform mixing can be realized easily, it is stabilized and it can produce the lithium secondary battery of a high charge-and-discharge capacity.

[0035]

[Example] Although the example and its example of a comparison of this invention are shown and the effectiveness is explained concretely hereafter, this invention is not restricted to the following example.

[0036] example 1 (production of lithium secondary battery) drawing 1 -- some cylindrical lithium secondary batteries -- a cross-section front view -- being shown -- 7 -- a positive electrode and 8 -- for a positive-electrode tab and 11, as for a positive-electrode lid and 13, a negative-electrode tab and 12 are [a negative electrode and 9 / a separator and 10 / a cell can and 14] gaskets. The lithium secondary battery shown in drawing 1 is the following, and was made and produced.

[0037] (Production of a positive electrode) the scale-like natural-graphite 7 weight section whose mean particle diameter is 1 micrometer as an electric conduction agent at the $LiCoO_2$ 88 weight section as positive active material, and the polyvinylidene fluoride 5 weight section addition as a binder -- carrying out -- this -- a N-methyl-2-pyrrolidone -- adding -- mixing -- a positive electrode -- the slurry of a mixture was prepared. subsequently, this positive electrode -- to the aluminium foil (25 micrometers in thickness) as a positive-electrode charge collector, it applied to both sides, the mixture was dried with the doctor blade method, and, subsequently pressing of the electrode was carried out with the roller press. It started by width of face of 40mm in the magnitude whose die length is 285mm, and the positive electrode 7 was produced. however, a part with a die length [of the both ends of a positive electrode 7] of 10mm -- a positive electrode -- a mixture was not applied, but aluminium foil was exposed, and the positive-electrode tab 10 was stuck to one of these by pressure by ultrasonic association.

[0038] (Production of a graphite particle)

(1) The 100 weight sections, the tar pitch 40 weight section, the silicon carbide 14 weight section whose mean particle diameter is 48 micrometers, and the coal tar 20 weight section were mixed, and it mixed at 200 ℃ for 1 hour in the end of a coke breeze whose mean diameter is 5 micrometers. The obtained mixture was ground and pressing was carried out to the pellet type, and subsequently, among nitrogen-gas-atmosphere mind, to 900 ℃, it heated, and using the Atchison furnace, it ranks second and graphitized [the temperature up was carried out and] to 3000 ℃. The graphite particle through and whose mean particle diameter are 20 micrometers about grinding and the screen of 200 meshes of openings using a hammer mill in the obtained graphitization object was produced. The bulk specific gravity of this graphite particle was 0.56. Moreover, the specific surface area by the BET adsorption method was $3.6m^2/g$. As a result of performing pore-volume-distribution measurement by the method of mercury penetration about

the obtained graphite particle, it had pore in the range of 0.01-100 micrometers, and total pore volume was 0.9cc/g. Moreover, as a result of selecting the obtained graphite particle as 100-piece arbitration and measuring an aspect ratio, it was 2.0 and the magnitude Lc (002) of 0.336nm and microcrystal of the distance d between layers of the crystal by the X-ray wide angle diffraction of a graphite particle (002) was 100nm or more. Furthermore, according to the scanning electron microscope (SEM) photograph of the obtained graphite particle, this graphite particle was having structure gathered or combined so that a flat-like particle might become un-parallel [two or more orientation side]. A sample is called for the graphite particle produced as mentioned above below.
[0039] (2) The needle coke powder 100 weight section of 20 micrometers of mean diameters, the tar pitch 10 weight section, and the coal tar 20 weight section were mixed at 230 ℃ for 1 hour. Subsequently, after calcinating this mixture at 1000 ℃ among nitrogen, it ground and powder with a mean particle diameter of 38 micrometers was produced. After graphitizing this powder at 3000 ℃ using the Atchison furnace further, through and a graphite particle were obtained for the screen of 200 meshes of openings. As a result of selecting the obtained graphite particle as 100-piece arbitration and measuring an aspect ratio, it was 2.5 and the magnitude Lc (002) of 0.336nm and microcrystal of the distance d between layers of the crystal by the X-ray wide angle diffraction of a graphite particle of a graphite particle (002) was 100nm or more. Furthermore, according to the scanning electron microscope (SEM) photograph of the obtained graphite particle, this graphite particle was having structure gathered or combined so that a flat-like particle might become un-parallel [two or more orientation side]. B sample is called for the graphite particle produced as mentioned above below.
[0040] (Measurement of the discharge capacity of a graphite particle) To 90 % of the weight of graphite particles, the polyvinylidene fluoride (PVDF) dissolved in the N-methyl-2-pyrrolidone was added 10% of the weight, was kneaded by solid content, and the graphite paste was produced. This graphite paste was applied to rolling copper foil with a thickness of 10 micrometers, and was dried further, and it considered as the negative electrode.
[0041] Constant current charge and discharge according the produced sample electrode to 3 terminal method were performed, and evaluation as a negative electrode for lithium secondary batteries was performed. Drawing 2 is the schematic diagram of the lithium secondary battery used for the experiment. The solution which dissolved $LiPF_6$ so that it might become with the concentration of one mol/l. at the mixed solvent of ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC:DMC=1:1 (volume ratio)) was put into the glass cell 1 as the electrolytic solution 2, the laminating of a sample electrode 3, a separator 4, and the counter electrode 5 was carried out, they have been arranged, and the reference electrode 6 was further hung from the upper part. The metal lithium was used for the counter electrode 5 and the reference electrode 6, and the polyethylene micropore film was used for the separator 4. By the constant current of 0.5 mA/cm2, it charged to 5mV (V vs Li/Li^+) and the trial which discharges to 1V (V vs Li/Li^+) was performed. The obtained result is shown in Table 1.
[0042]
[Table 1]

sample	Sample A	Sample B
Discharge capacity (mAh/g)	350 (100)	340 (97)
Irreversible capacity (mAh/g)	35	25

( ):compare A:100%

The A sample 90 weight section and the B sample 10 weight section are mixed to homogeneity. (Production of a negative electrode) Subsequently, this mixed graphite and PVDF as a binder are mixed by the ratio of the weight ratio 90:10. both sides of the copper foil (10 micrometers in thickness) as a negative-electrode charge collector after making a solvent (N-methyl-2-pyrrolidone) distribute this and considering as a slurry -- a doctor blade method -- applying -- desiccation -- subsequently, with the roller press, pressing of the electrode was carried out and it considered as the negative electrode. It started by width of face of 40mm in the magnitude whose die length is 290mm, and the negative electrode 8 was produced. this negative electrode -- a positive electrode -- the same -- a negative electrode with a die length [of both ends] of 10mm -- the negative-electrode tab 11 was stuck to one side of the part to which the mixture is not applied by pressure by ultrasonic jointing.

[0043] (Preparation of the electrolytic solution) $LiPF_6$ [1 mol /l] was dissolved in volume mixed solvents, such as ethylene carbonate and dimethyl carbonate,., and the electrolytic solution was prepared.

[0044] (Production of a cell) After carrying out the laminating of the separator 9 which consists of said positive electrode 7 and a porosity film made from polyethylene (thickness of 25 micrometers, width of face of 44mm), and said negative electrode 8 in this sequence, respectively, it wound around the curled form and the electrode group was produced so that said negative electrode might be located outside. This electrode group was contained with the cell can 13 made from stainless steel, respectively, can bottom welding of the negative-electrode tab 11 was carried out, and the converging section for closing the positive-electrode lid 12 was formed. Then, after pouring said electrolytic solution into the cell can 13, the positive-electrode tab 10 was welded to the positive-electrode lid 12, and the cylindrical lithium secondary battery was assembled for the positive-electrode lid 12 in total.

[0045] The cylindrical lithium secondary battery was assembled like the example 1 except having made the compounding ratio of A sample in example 2 negative-electrode production, and B sample into 80 weight sections and 20 weight sections, respectively.

[0046] The cylindrical lithium secondary battery was assembled like the example 1 except having made the compounding ratio of A sample in example 3 negative-electrode production, and B sample into 70 weight sections and 30 weight sections, respectively.

[0047] The cylindrical lithium secondary battery was assembled like the example 1 except having made the compounding ratio of A sample in example 4 negative-electrode production, and B

sample into 60 weight sections and 40 weight sections, respectively.
[0048] The cylindrical lithium secondary battery was assembled like the example 1 except having made the compounding ratio of A sample in example 5 negative-electrode production, and B sample into 50 weight sections and 50 weight sections, respectively.
[0049] The cylindrical lithium secondary battery was assembled like the example 1 except having made the compounding ratio of A sample in example of comparison 1 negative-electrode production, and B sample into the 100 weight sections and 0 weight section, respectively.
[0050] The cylindrical lithium secondary battery was assembled like the example 1 except having made the compounding ratio of A sample in example of comparison 2 negative-electrode production, and B sample into 0 weight section and the 100 weight sections, respectively.
[0051] Instead of A sample, using the scale-like artificial-graphite powder which is 20 micrometers, mean particle diameter made the compounding ratio this artificial-graphite powder 70 weight section and the B sample 30 weight section, and produced the cylindrical lithium secondary battery like the example 1 hereafter in example of comparison 3 negative-electrode production. The bulk specific gravity of this artificial-graphite powder was 0.24, and the discharge capacity and irreversible capacity which were measured independently were 340 mAh/g (the sample ratio for B: 101%), and 85 mAh/g, respectively.
[0052] The needle coke powder 100 weight section of 20 micrometers of example of comparison 4 mean diameters, the pitch 10 weight section, and the coal tar 20 weight section were mixed at 230 ℃ for 1 hour. Subsequently, after grinding and fabricating this mixture, the Atchison furnace was used for baking and a pan at 1000 ℃ among nitrogen, and it graphitized at 3000 ℃. The acquired graphite Plastic solid was pulverized and through and a graphite particle were obtained for the screen of 200 meshes of openings. The bulk density of the obtained graphite particle, mean particle diameter, specific surface area, d (002) and Lc (002), and an aspect ratio were 0.336nm, 100nm or more, and 2.3, respectively. As a result of observing the obtained graphite particle with an electron microscope, the flat-like particle was having massive structure combined [which combined together and gathered]. Moreover, the discharge capacity and irreversible capacity which were measured by independent [of this graphite particle] were 343 mAh/g and 20 mAh/g, respectively. The negative electrode was produced as this graphite particle 30 weight section and the A sample 70 weight section, and the cylindrical lithium secondary battery was hereafter produced like the example 1.
[0053] After grinding an example of comparison 5 mesophase pitch in mean particle diameter of 32 micrometers and carrying out oxidation treatment at 300 ℃, it calcinated at 1000 ℃ among nitrogen. Subsequently, through and a graphite particle were obtained [this powder] for the screen of 200 meshes of openings after graphitization at 3000 ℃ using the Atchison furnace. The bulk density of the obtained graphite particle, mean particle diameter, specific surface area, d (002) and Lc (002), and an aspect ratio were 0.336nm, 100nm or more, and 1.8, respectively. As a result of observing the obtained graphite particle with an electron microscope, massive particle shape was carried out. Moreover, the discharge capacity and irreversible capacity which were measured by independent [of this graphite particle] were 330 mAh/g and 18 mAh/g, respectively. The negative electrode was produced as this graphite particle 30 weight section and the A sample 70 weight section, and the cylindrical lithium secondary battery was hereafter produced like the example 1.
[0054] About the lithium secondary battery of the acquired examples 1-5 and the examples 1-5 of a comparison, the charge termination electrical potential difference was set to 4.15V, discharge

final voltage was set to 2.8V, the charge and discharge current was changed in 200 to 800mA, and the discharge capacity at the time of rapid charge and discharge was measured. The result is shown in drawing 3 , using discharge capacity at the time of 200mA of charge and discharge currents of the example 1 of a comparison as 100%. Moreover, the charge-and-discharge cycle property of each cell was measured as 200mA of charge and discharge currents. The result is shown in drawing 4 , using discharge capacity at the time of one cycle of the example 1 of a comparison as 100%.

[0055] The rapid charge-and-discharge property of an example is good as compared with the example of a comparison, and is understood that there are very few falls of discharge capacity also in a big charge and discharge current so that more clearly than drawing 3 . Moreover, even if the cycle property of an example is good as compared with the example of a comparison and it passes through the high number of cycles, it turns out that a big discharge capacity is maintainable, so that more clearly than drawing 4 .

[0056]

[Effect of the Invention] As explained above, according to this invention, there are many occlusion and burst sizes of the lithium at the time of performing charge and discharge by the high charge and discharge current especially, and charge-and-discharge capacity is large, and the fall of the charge-and-discharge capacity by the charge-and-discharge cycle can obtain few lithium secondary batteries.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] some cylindrical lithium secondary batteries -- it is a cross-section front view.

[Drawing 2] It is the schematic diagram of the lithium secondary battery used for the experiment.

[Drawing 3] It is the graph which shows the relation of the charge and discharge current and discharge capacity in the rapid charge and discharge test of the lithium secondary battery of examples 1-5 and the examples 1-5 of a comparison.

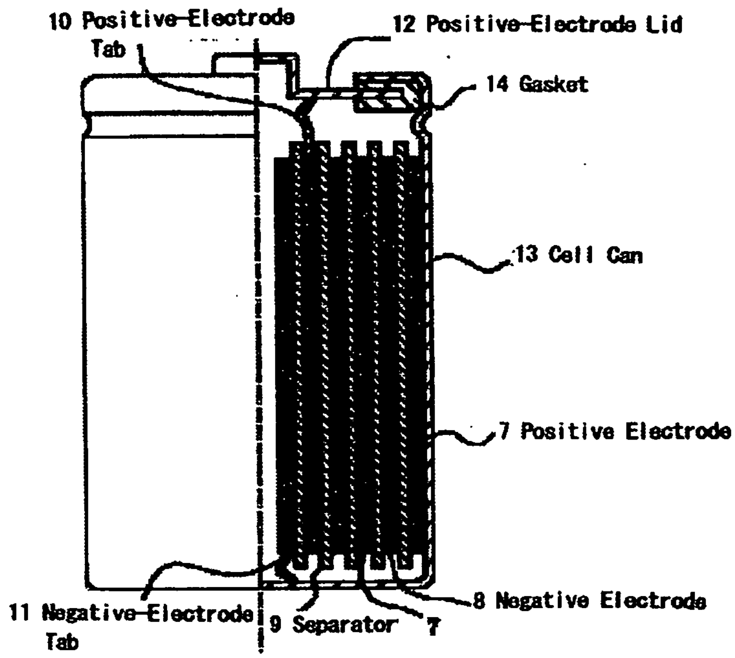
[Drawing 4] It is the graph which shows the relation of the number of cycles and discharge capacity in the cycle trial of the lithium secondary battery of examples 1-5 and the examples 1-5 of a comparison.

[Description of Notations]

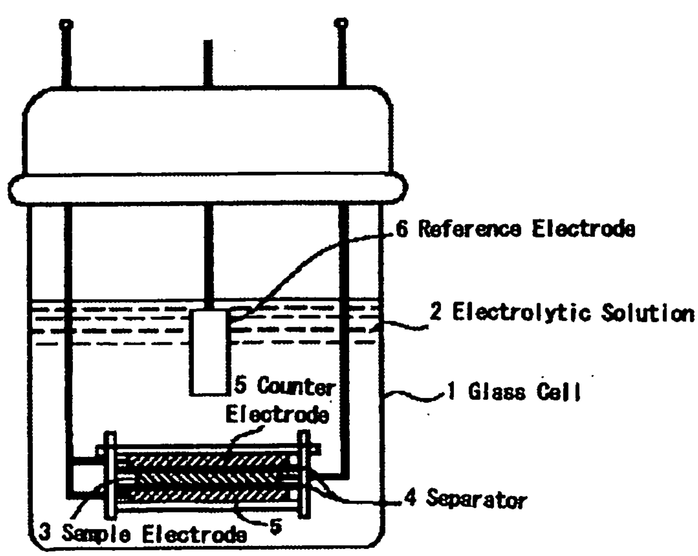
1 Glass Cell
2 Electrolytic Solution
3 Sample Electrode
4 Separator
5 Counter Electrode
6 Reference Electorode
7 Positive Electrode
8 Negative Electrode
9 Separator
10 Positive-Electrode Tab
11 Negative-Electrode Tab
12 Positive-Electrode Lid

13 Cell Can
14 Gasket

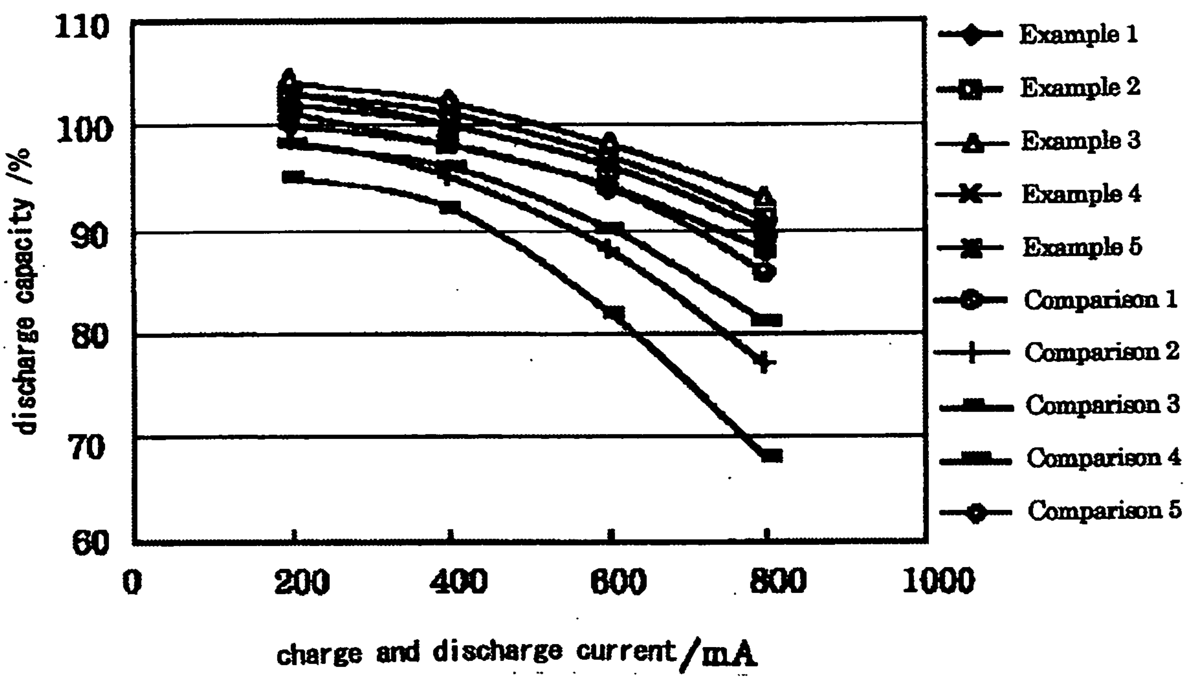
[Drawing 1]



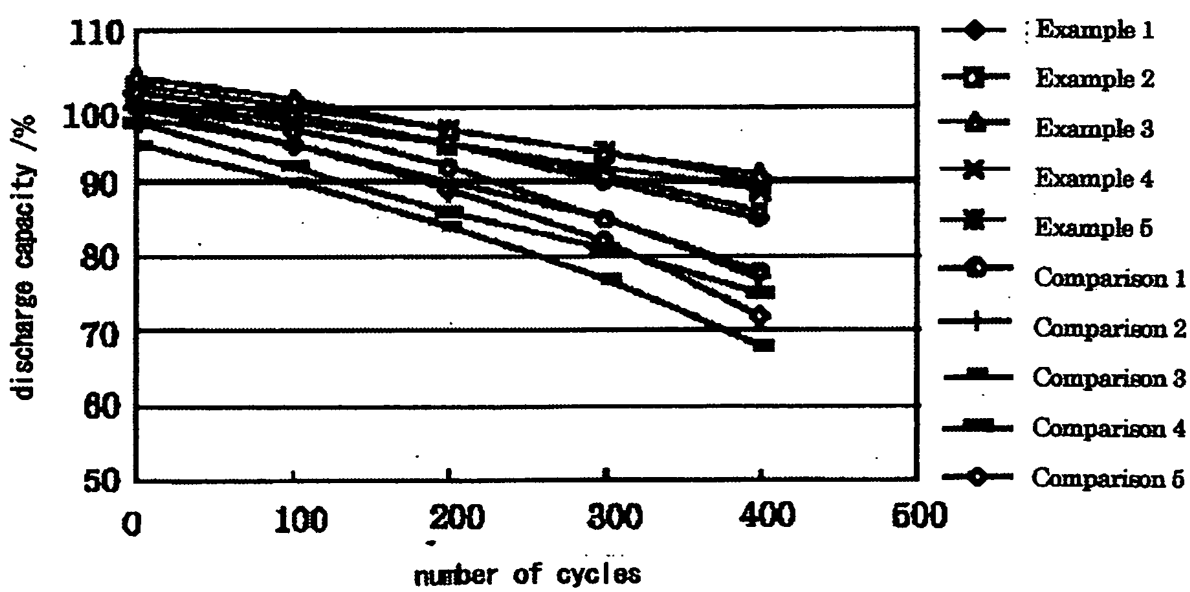
[Drawing 2]



[Drawing 3]



[Drawing 4]



* NOTICES *